# LA-UR-23-29726

**Approved for public release; distribution is unlimited.**

| | |
|---|---|
| **Title:** | Journey to Differentiable Models: Chemical Bonding, Electronic Structure and Machine Learning |
| **Author(s):** | Fedik, Nikita |
| **Intended for:** | Invited seminar at North Dakota State University |
| **Issued:** | 2023-08-23 |



# Journey to Differentiable Models: Chemical Bonding, Electronic Structure and Machine Learning

Nikita Fedik
Director's Postdoc Fellow
T-1/CNLS



NDSU 2023

# Acknowledgments


- Prof. Alexander Boldyrev

- Prof. Kit H. Bowen

- Prof. Alvaro Muñoz-Castro

- Dr. Sergei Tretiak (T-1)
- Dr. Ben Nebgen (T-1)
- Dr. Kipton Barros (T-1)
- Dr. Maksim Kulichenko (T-1)
- Dr. Richard Messerly (T-1)
- Dr. Nicholas Lubbers (CCS-3)
- Dr. Ying Wai Li (CCS-7)

- Prof. Oleksandr Isayev
- Dr. Roman Zubatyuk

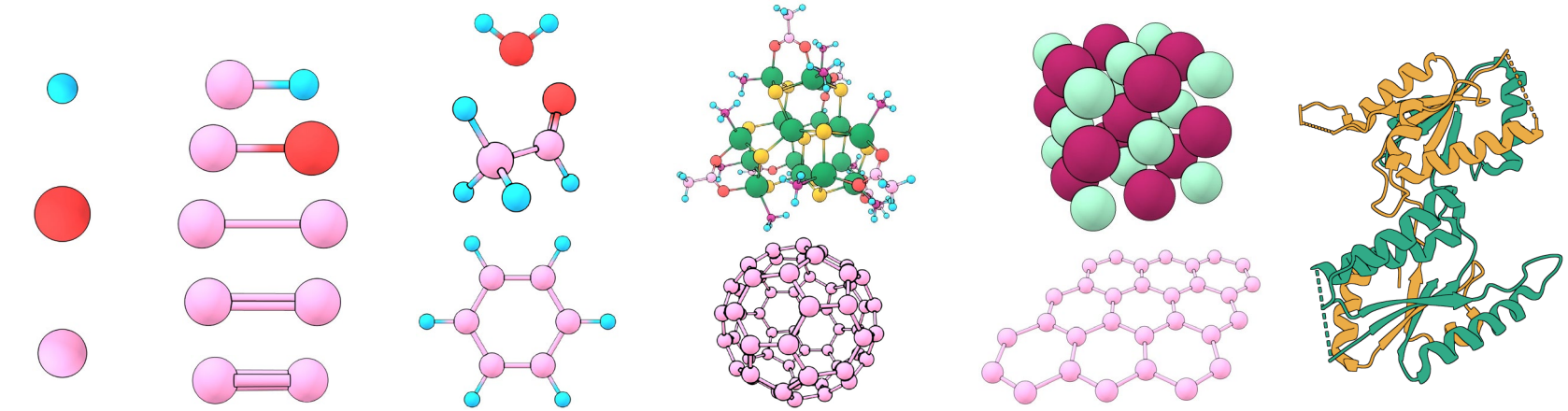
- Dr. Justin S. Smith

$ LDRD funding

$ Director's Fellowship

$ CNLS support

# Coarse Atomistic Scale: Chemist's Perspective



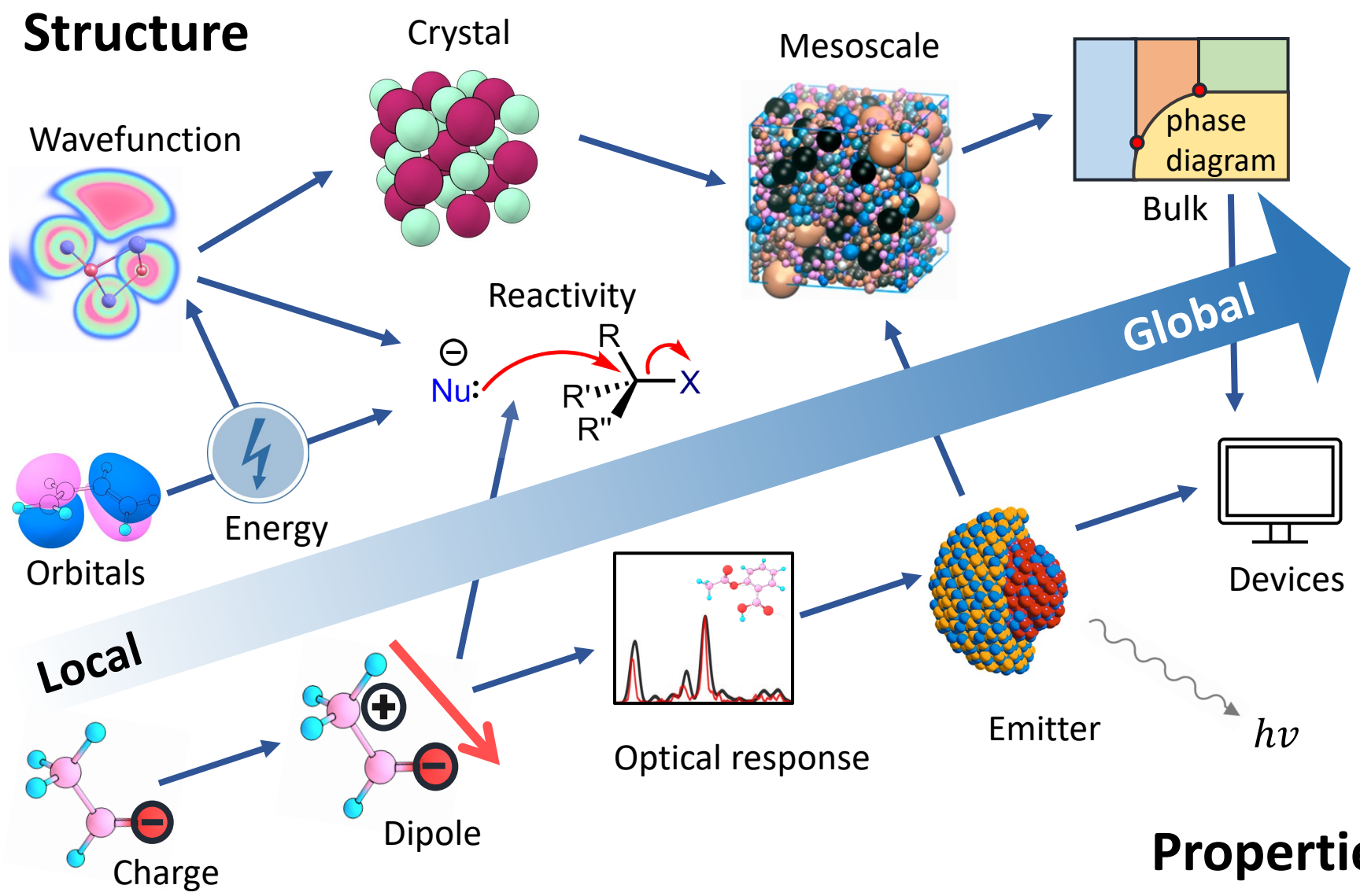
atoms | bonds | molecules | nanoparticles | 2D and 3D structures | proteins

Complexity

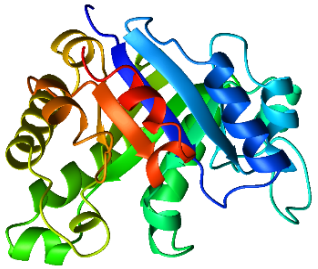
| Local properties | | Global properties | | | |
|---|---|---|---|---|---|
| Atomic energy | Atomic charge | Total energy | Orbital energies | Electron density | Dipoles |
| Bond order | | Reactivity | Band gap | Electron excitation | Transport |

- local and global properties – core of the chemical mindset and vocabulary
- analysis: $\sum$ local contributions $\approx$ global property, and vice versa

# Chemical Discovery



# Chemical Discovery on Different Scales



proteins
$10^6$–$10^9$ atoms

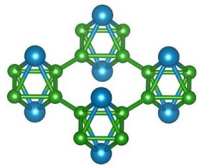
classical
$\mathcal{O}(n)$

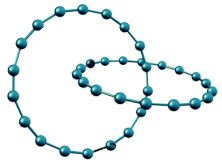
reduced QM+ML

chemical bonding

molecules
10–$10^3$

tight-binding
$\mathcal{O}(n) - \mathcal{O}(n^2)$





DFT
$\mathcal{O}(n^2) - \mathcal{O}(n^3)$

CCSD(T)
$\mathcal{O}(n^7)$

machine
learning

$H_2O$

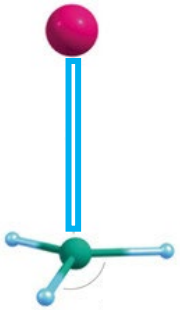
exact solution

$\sim \exp(n)$

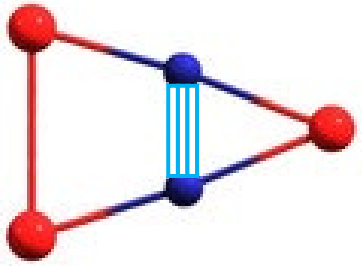
...

error

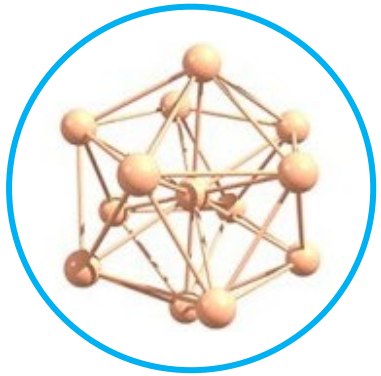
log cost



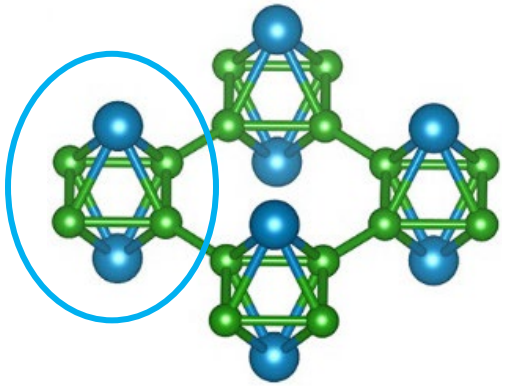
$NaBH_3^-$



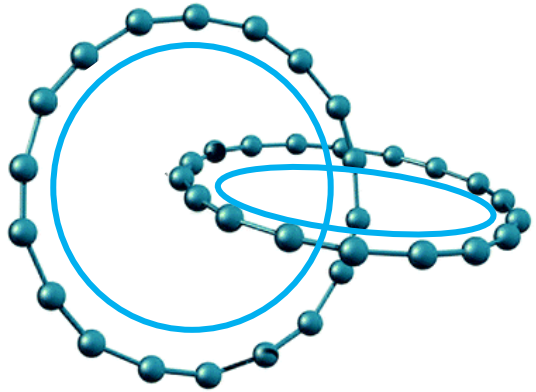
$B_2Al_3^-$



Au cages



$B_4X_2$ monolayers



interlocked $C_{18}$ rings

*delocalization*

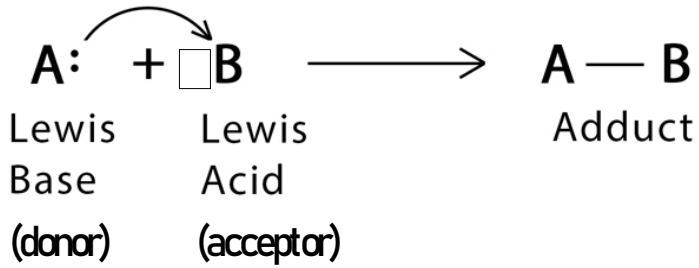
single 2e-2c

delocalized over all atoms: 2e-nc bonds

# Forcing Electron Where It Doesn't Belong

Electron transfer is ubiquitous:

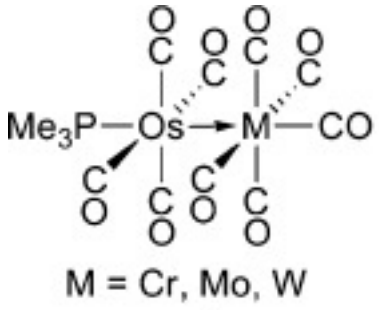
- solvation
- catalytic reactions
- biochemical systems

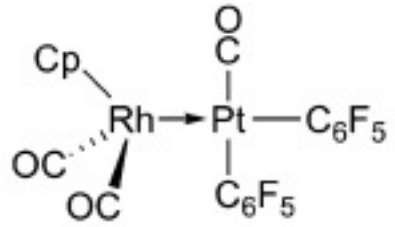



Classic example

$$H_3N: + BH_3 \rightarrow H_3N \rightarrow BH_3$$

some transition metals function as Lewis bases (donors)

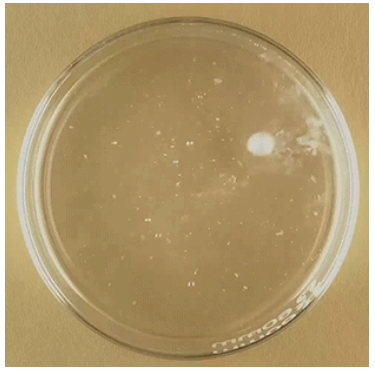



## Can alkali metals (Na) react as Lewis bases?

$$Na^- \rightarrow X$$

- Na always tends to become $Na^+$



in water:

$$2Na + 2H^+ \rightarrow 2Na^+ + H_2 + \text{energy!}$$

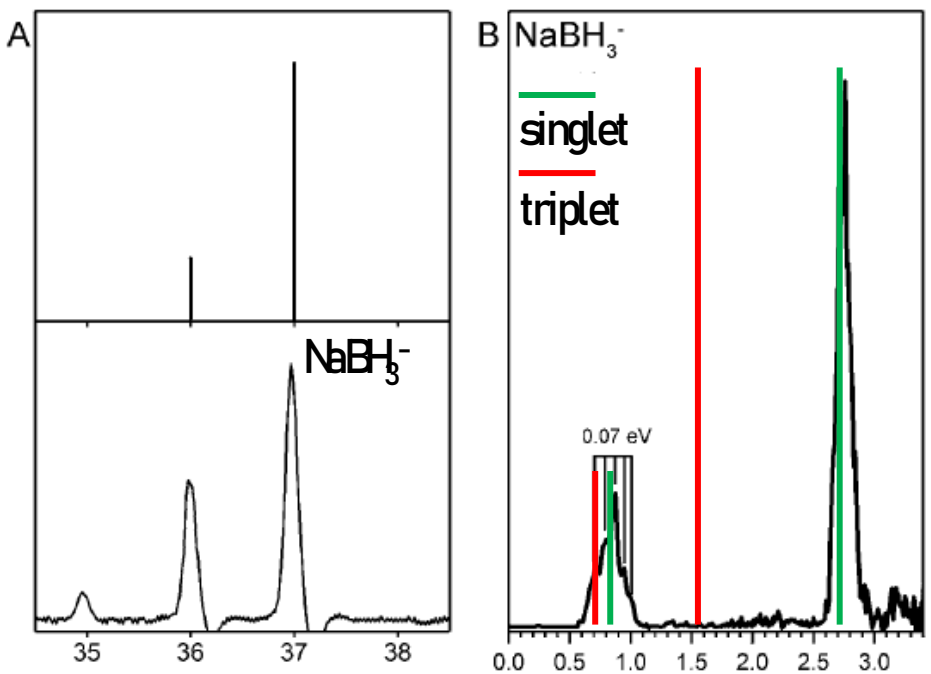
- $Na^-$ would be a donor
- we need a pair X that avoids electron even more than Na
- electron affinities:

| | |
|---|---|
| Na | 0.54 eV |
| $BH_3$ | 0.38 eV |

$Na^- \rightarrow X$ or $Na\text{-}X^-$ ?

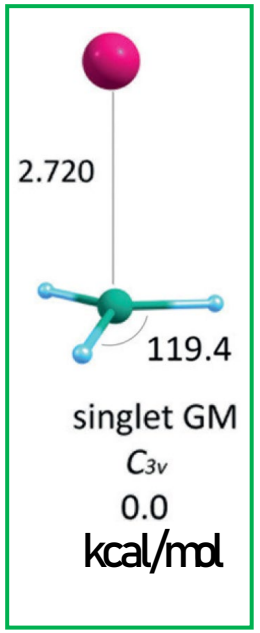
# Synergy of Theory and Experiment

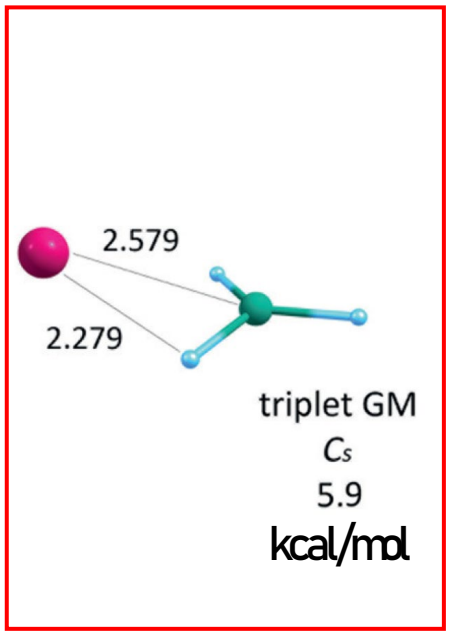
synthesis of anionic cluster – laser vaporization → experimental mass- and photoelectron spectra → computational PES exploration → global minimum identification based on VDEs → bonding analysis

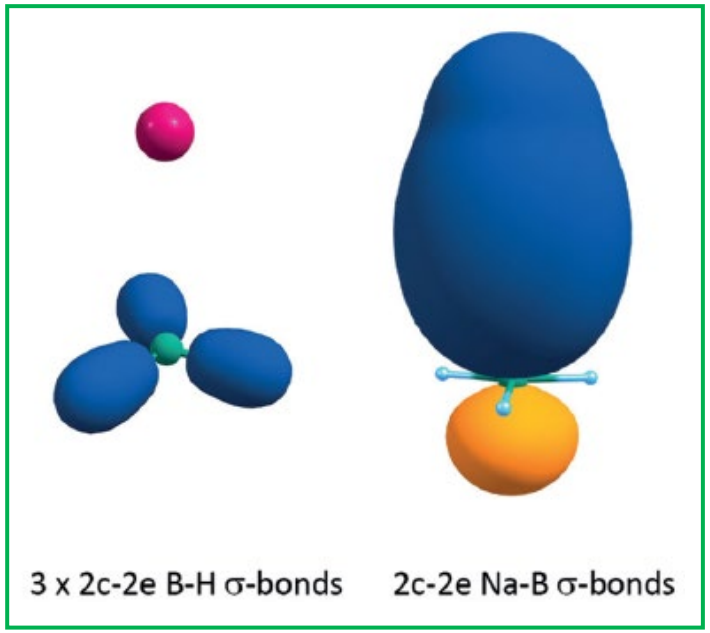



mass, amu

vertical detachment energy (VDE), eV



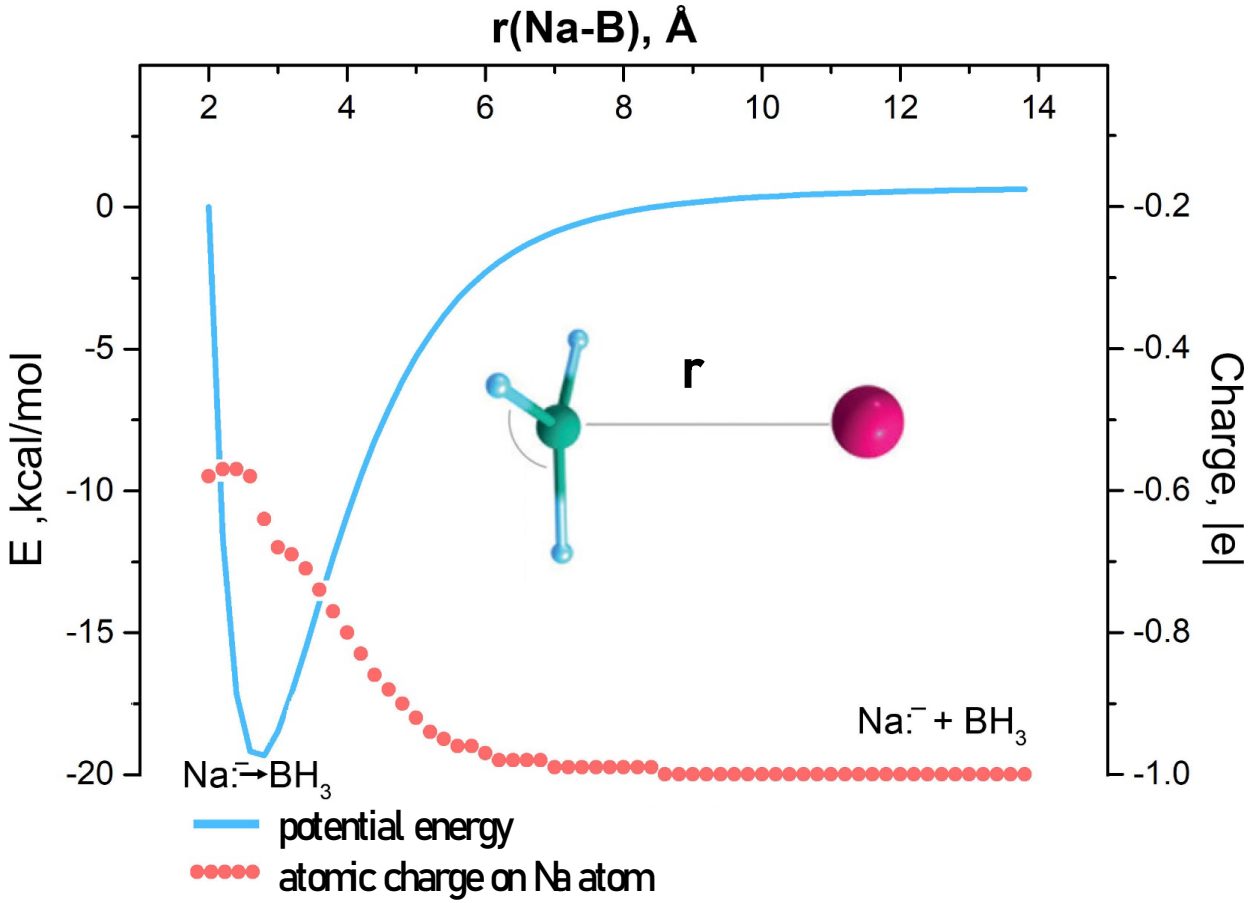




direct Na–B bond

experiment by K. Bowen (Johns Hopkins University)

# Want to Understand the Bond? Break It!

| Dissociation pathway | BDE |
|---|---|
| $(Na\text{-}BH_3)^- \rightarrow Na:^- + BH_3$ | 17.8 |
| $(Na\text{-}BH_3)^- \rightarrow Na^{\cdot} + {}^{\cdot}BH_3^-$ | 30.1 |
| $(Na\text{-}BH_3)^- \rightarrow Na^+ + :BH_3^{2-}$ | 248.7 |
| $H_3N\text{-}BH_3 \rightarrow :NH_3 + BH_3$ | 26.0 |




From IUPAC Gold Book:

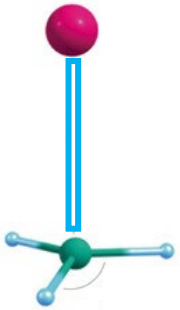
"The distinctive feature of dative bonds is that their minimum-energy rupture in the gas phase or in inert solvent follows the heterolytic bond cleavage path."

Electron affinities:

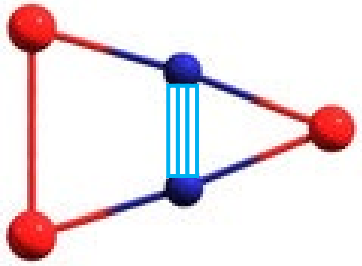
Na 0.54 eV
$BH_3$ 0.38 eV

High-impact in community:
25+ follow-up papers
broad discussion on dative bond

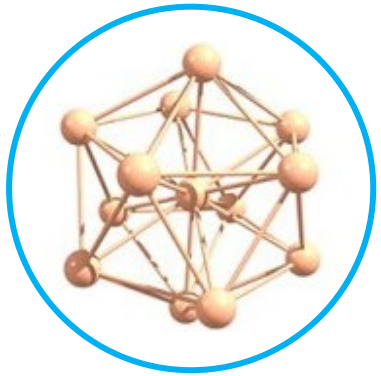
G. Liu, Fedik N, C. Martinez-Martinez, S. Ciborowski, X. Zhang, A. I. Boldyrev, K. Bowen, *Angewandte Chemie*, 2019, *58*, 13789-13793 (MP article)



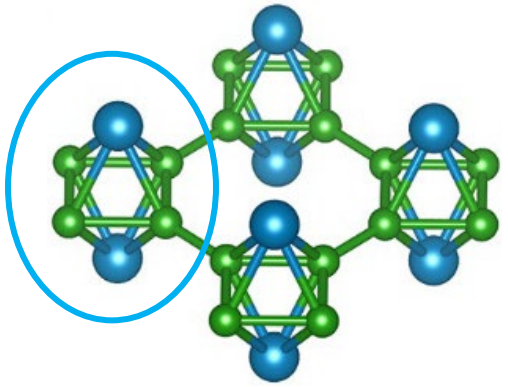
$NaBH_3^-$



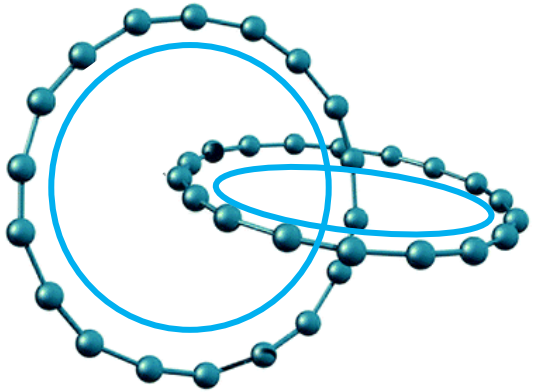
$B_2Al_3^-$



Au cages



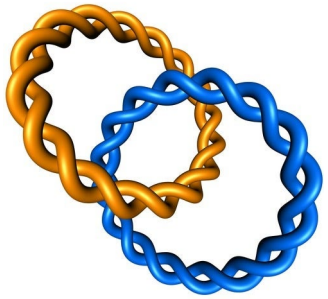
$B_4X_2$ monolayers



interlocked $C_{18}$ rings

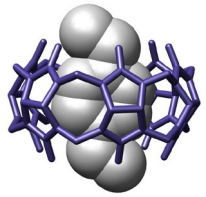
*delocalization*

# Exotic Topologies of Carbon



catenane

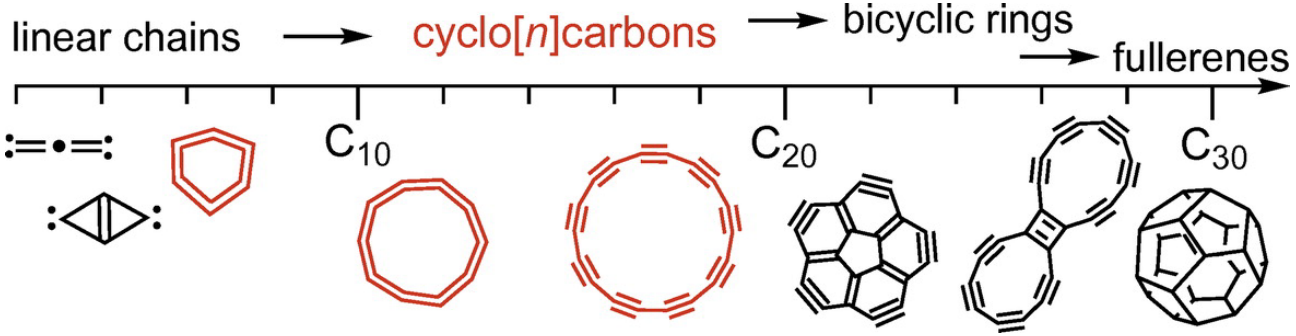
host-guest systems



molecular machines

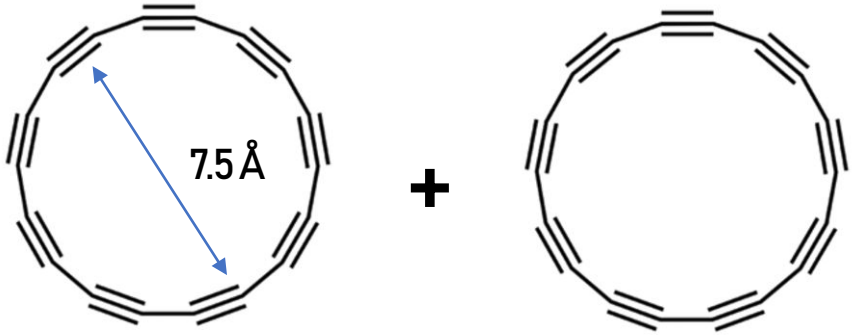
- very expensive synthetic effort
- ring topologies are very rare
- new candidate, cyclo[18]carbon, was synthesized in 2019

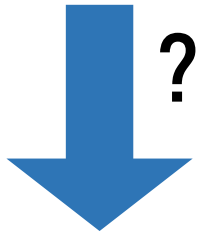
Kaiser *et all*, *Science*, **2019**, *365*, 299-1301

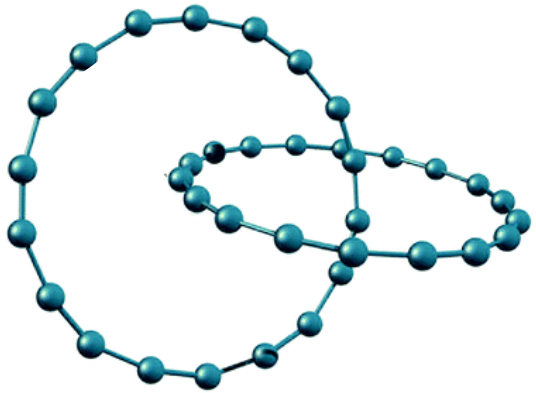



cyclo[18]carbon

my idea: can we mechanically interlock the rings?

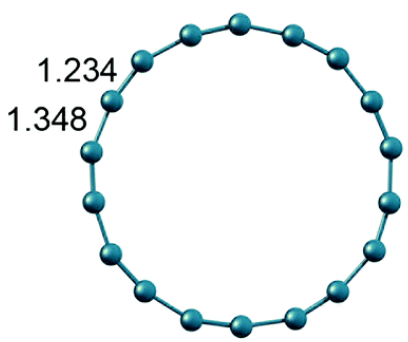


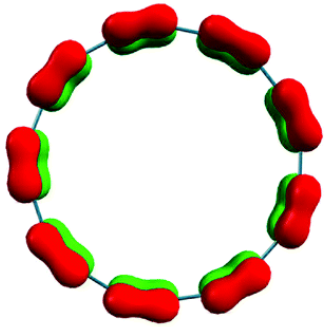
# Mechanical Bond?

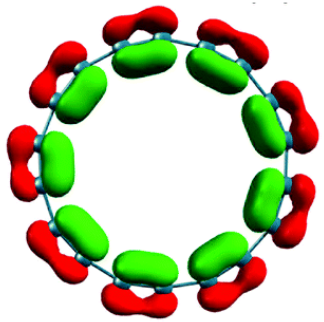
## single ring




$C_{9h}$

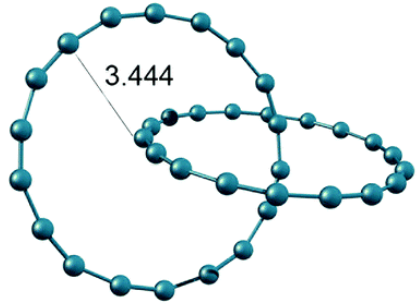
18 x 2c-2e C-C σ–bonds



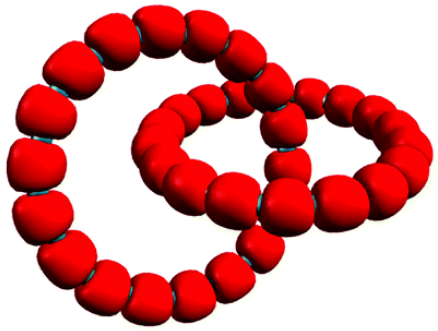


2 orthogonal sets of 9 x 2c-2e C-C π–bonds

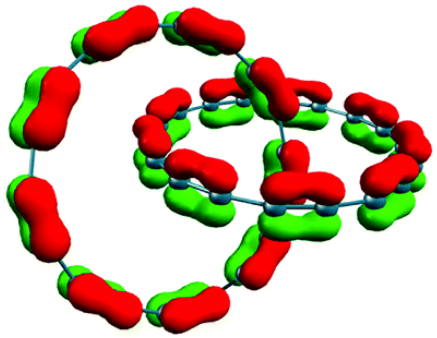
## interlocked rings

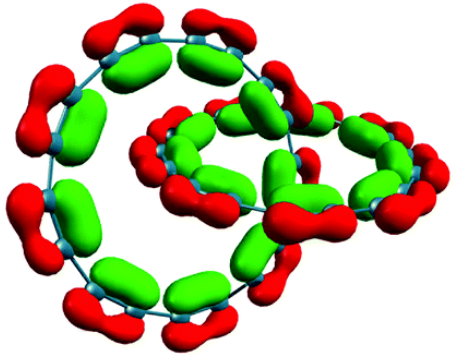



$C_1$



36 x 2c-2e C-C σ–bonds

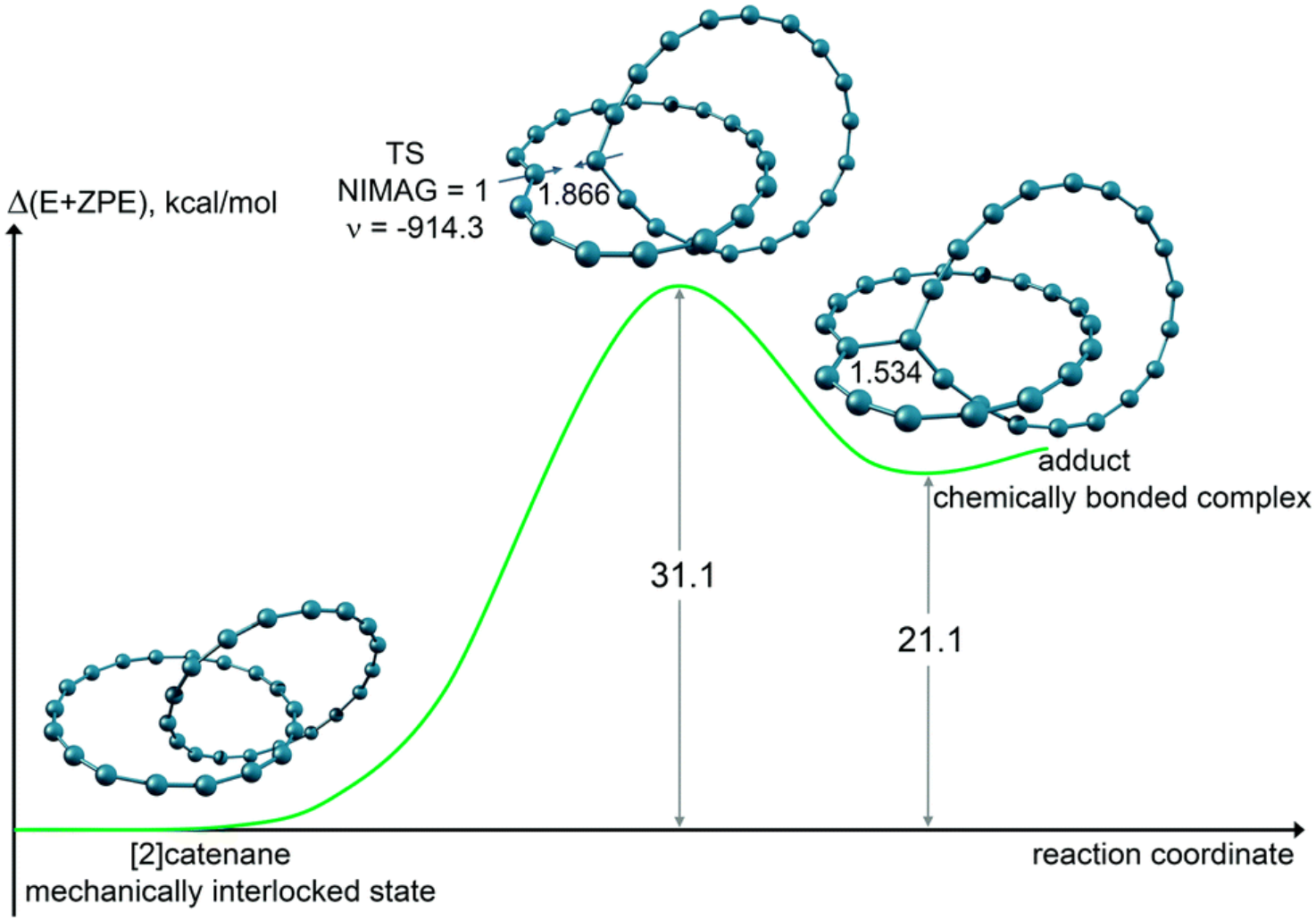


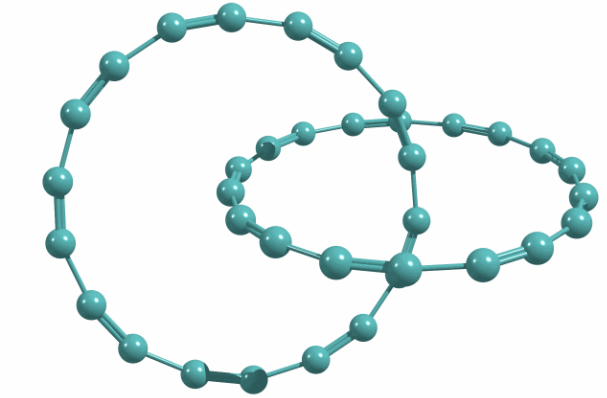


2 x 2 orthogonal sets of 9 x 2c-2e C-C π–bonds

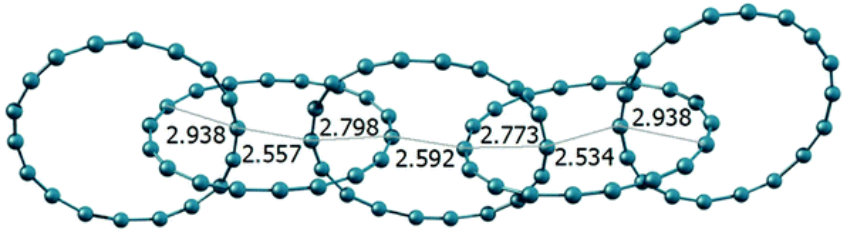
mechanical bond – no chemical bonds between rings

# Escaping Kinetic Trap

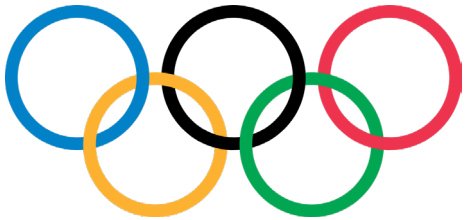


- rotational barrier <1 kcal/mol
- room temperature molecular gear



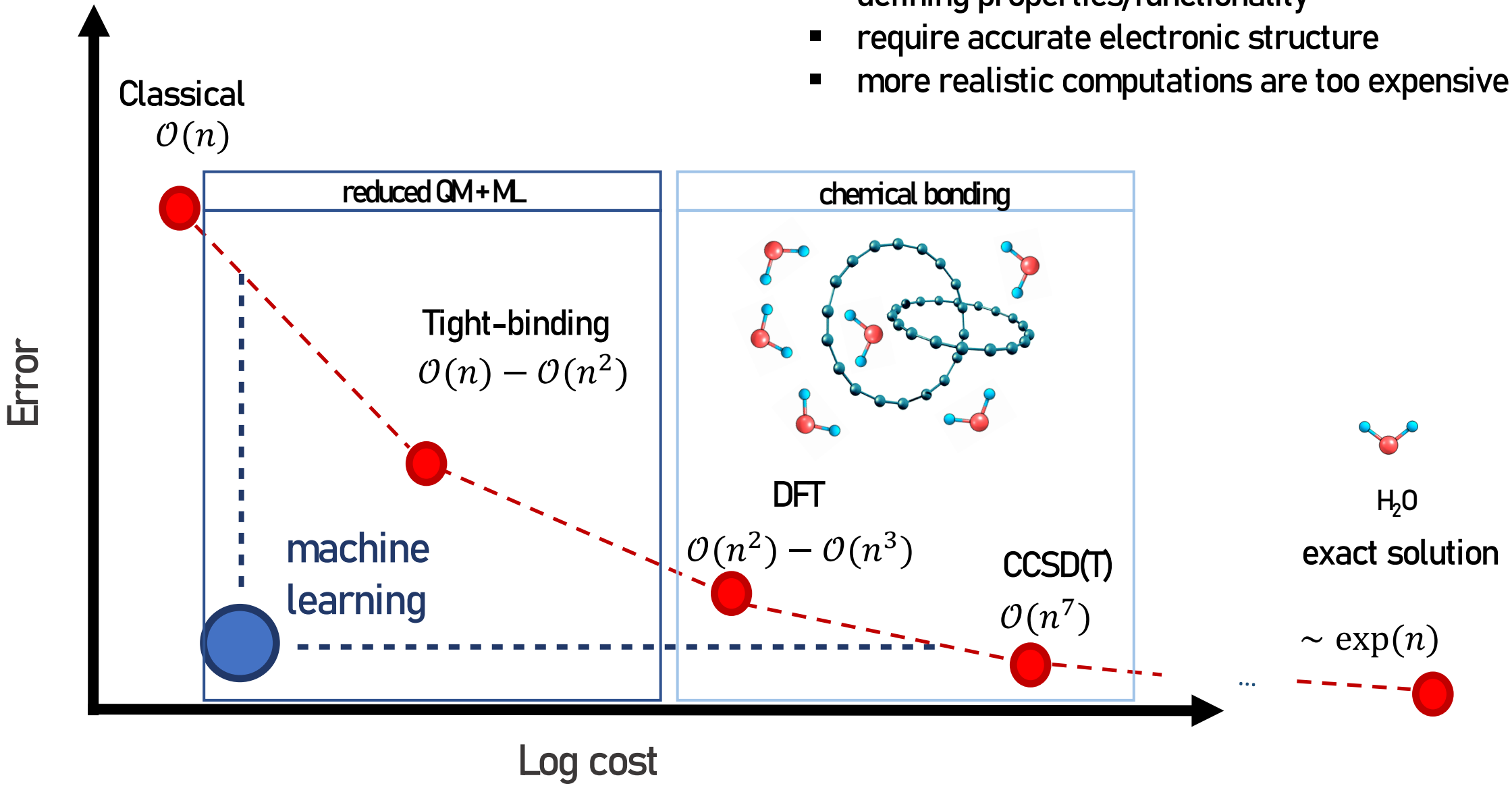

olympic rings?



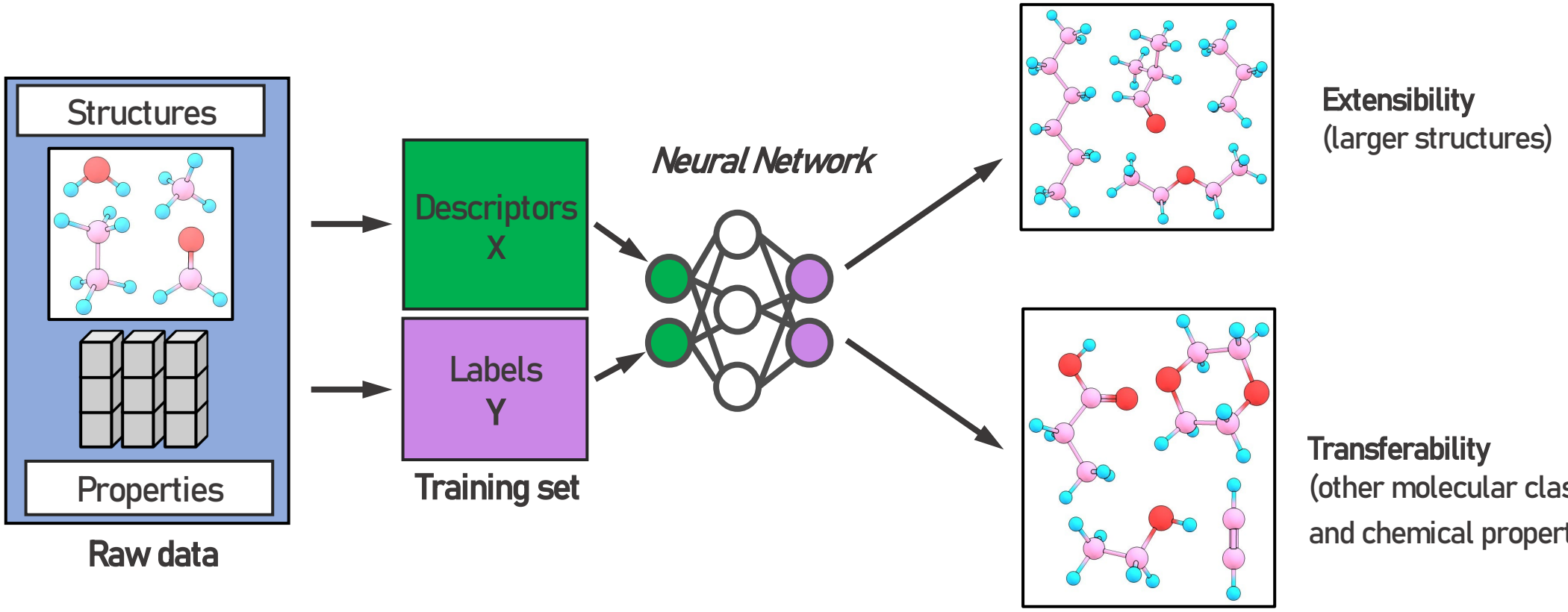
N Fedik, M Kulichenko, D. Steglenko, Alexander I. Boldyrev
*Chem Commun*, 2020, *56*, 2711-2714.

# Chemical Discovery on Different Scales

- chemicals bonds – fundamental building blocks defining properties/functionality
- require accurate electronic structure
- more realistic computations are too expensive



# Learning Chemical Properties without Electronic Structure




- ML establishes structure⇔property relationship
- "surrogate" models – no electronic structure

- training = minimization of the error: $\Delta(Y - Y^{ref})$
- loss function (e.g., RMSE) tracks error

$$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(Y_i - Y_i^{\mathrm{ref}})^2}$$

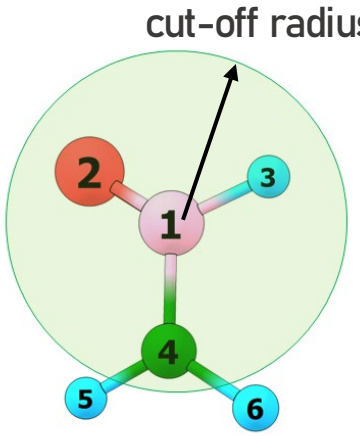
N. Fedik, R. Zubatyuk, M. Kulichenko, N. Lubbers, J. Smith, B. Nebgen, R. Messerly, Y. W. Li, A. Boldyrev, K. Barros, O. Isayev, S. Tretiak. 2022, *Nature Reviews Chemistry*, 6, 653-672

# Spatial Locality and Message-Passing

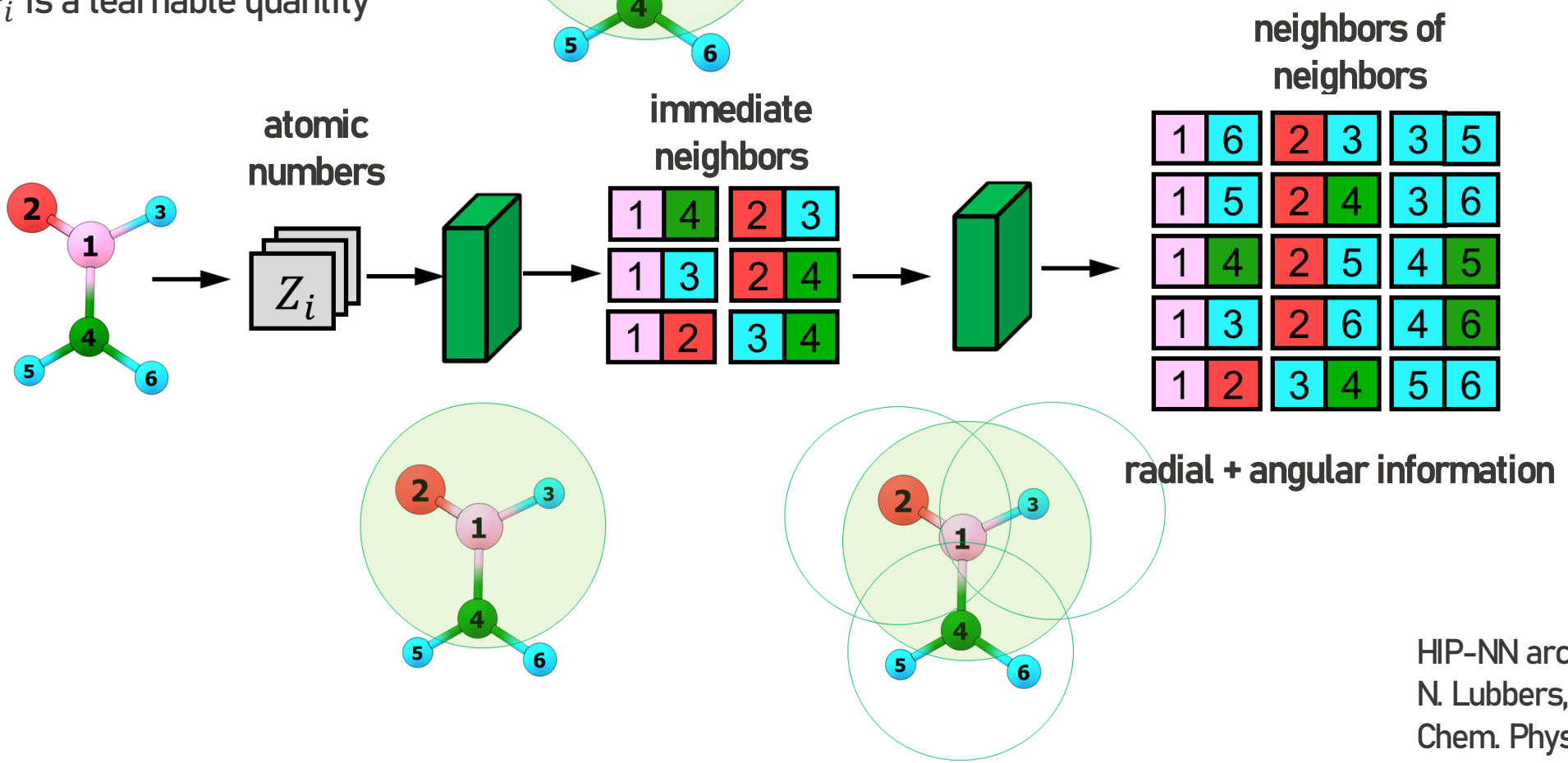
Local decomposition ansatz:

$$P^{\text{ref}} \approx P = \sum_{i=1}^{Natoms} P_i$$

- $P_i$ is a learnable quantity

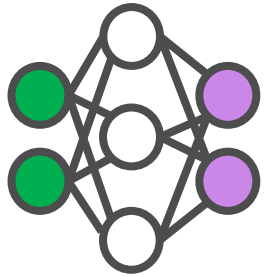


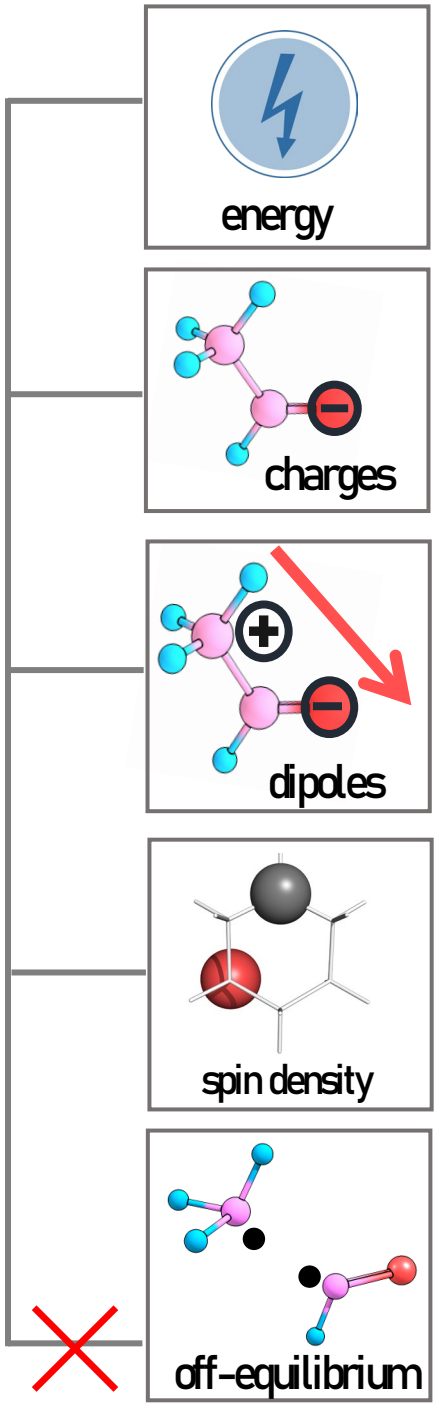

- locality is both bless (linear scaling) and curse (no long-range effects)
- message-passing propagates beyond radius and captures radial and angular information of distant atoms
- 2-passes are almost always enough for molecules

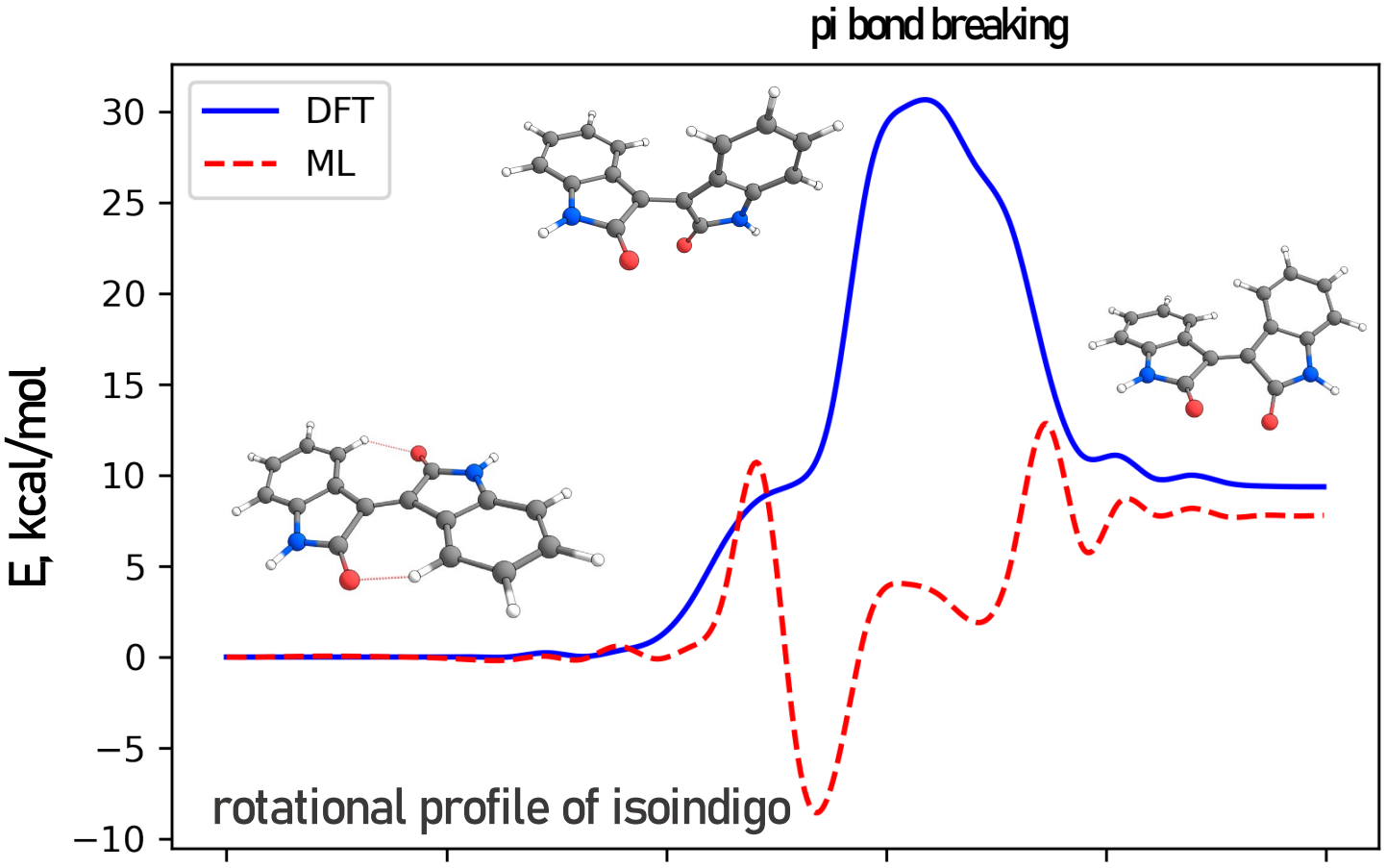


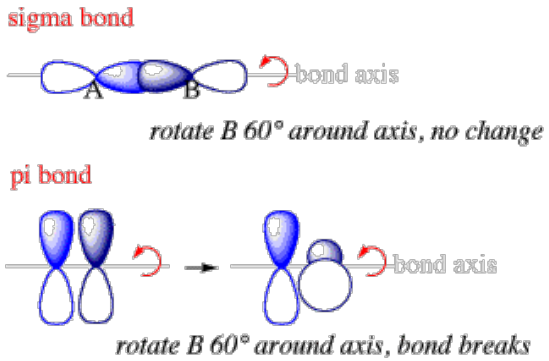

HIP-NN architecture
N. Lubbers, K. Barros, J. Smith, J. Chem. Phys. 148, 241715 (2018)

# Why Bonds Matter in ML



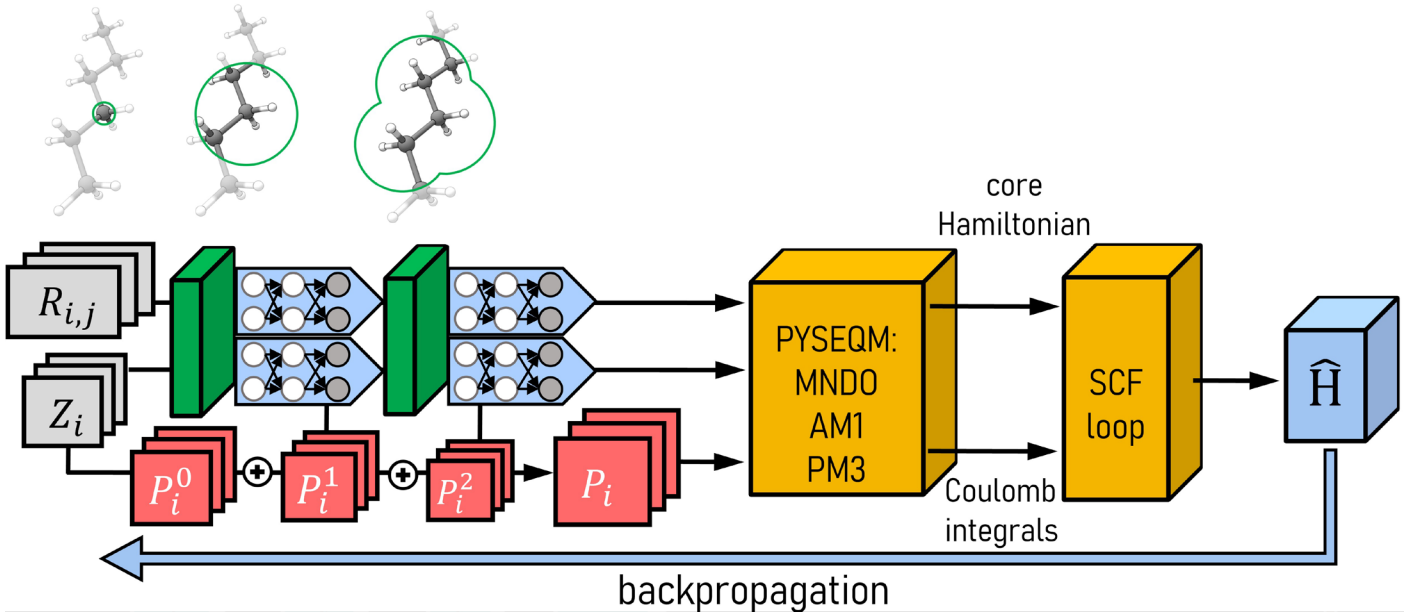



- ML potentials often fail near reactive regions (no electrons, datasets lack rare events)
- keeping QM would naturally describe off-equilibrium phenomena

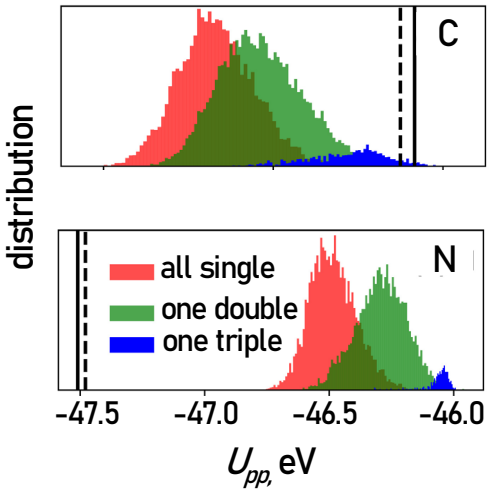
# PYSEQM: Electronic Structure improved by ML



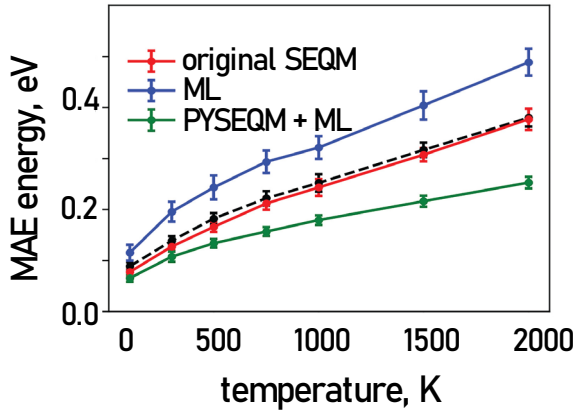

$$P_i = P_i^{SEQM} + \sum_n P_i^n = P_i^{SEQM} + \sum_n \left( \sum_a w_a^n \, z_{i,a}^n + B^n \right)$$

- PYSEQM: Pytorch Semiempirical Quantum Mechanics
- differentiable physics model – all gradients are available
- only 60k datapoints – physics is already there!
- interatomic potentials often require ~500k and more points
- highly transferable and extensible

original: parameters depend only on atom type PYSEQM: parameters depend on atom type + neighbors awareness of chemical bonding

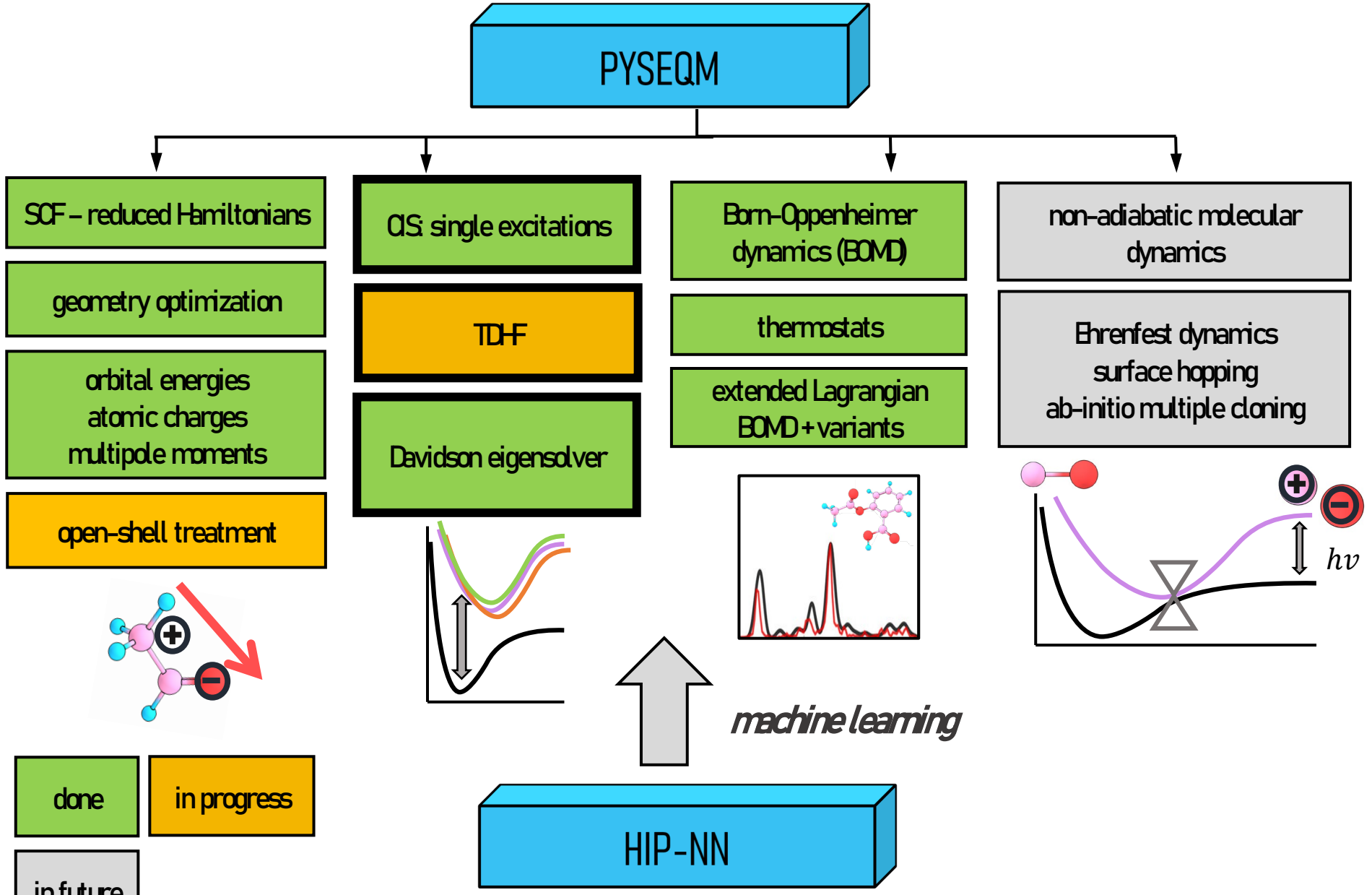



high-temperature molecular dynamics




G. Zhou et al, Deep learning of dynamically responsive chemical Hamiltonians with semiempirical quantum mechanics, *PNAS*, 2022, 119 (27) e2120333119

# PYSEQM: Modular Architecture




**Features:**

- modular architecture
- Pytorch backend
- automatic differentiation
- direct interface to ML
- batch GPU execution

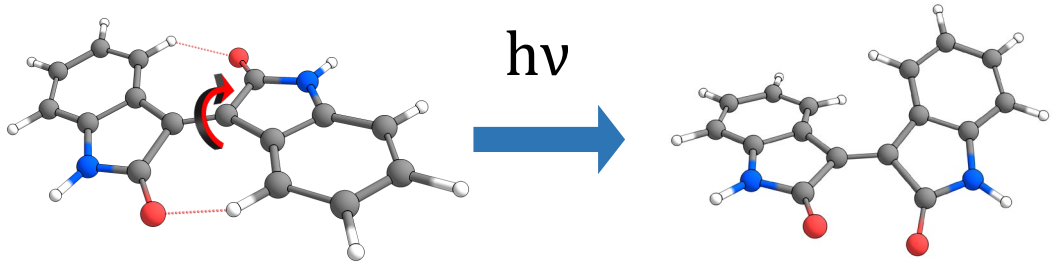
**Developers:**

- Maksim Kulichenko
- Nikita Fedik
- Guoqing Zhou
- Ben Nebgen
- Nicholas Lubbers
- Kipton Barros
- Walter Malone
- Anders Niklasson
- Yu Zhan
- Xinyang Li
- Sergei Tretiak

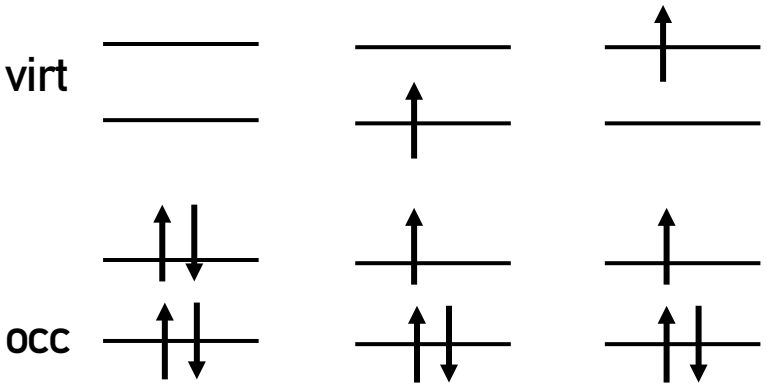
**Codes**

https://github.com/lanl/PYSEQM
https://github.com/lanl/hippynn
https://github.com/lanl/NEXMD

# Beyond Ground State



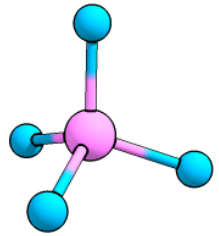

- ground state can only describe small fraction of chemistry
- simple model: CIS accounts for single excitations



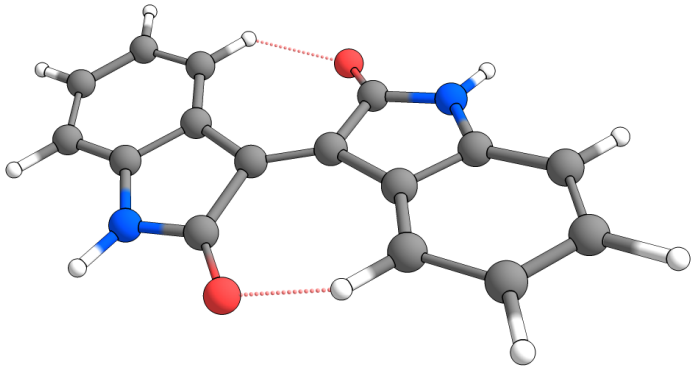

$$AX = \Lambda X, \; where \; (\lambda_i, \ldots \lambda_n) = excitation \; energies$$

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia||jb)$$

PYSEQM, CIS-PM3 | excitation energies in eV



```
7.914
8.583   8.583   8.583
10.087  10.087  10.087
```

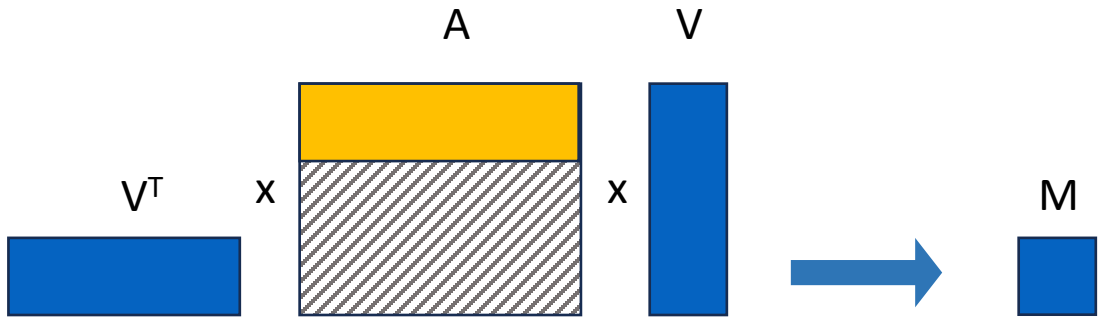


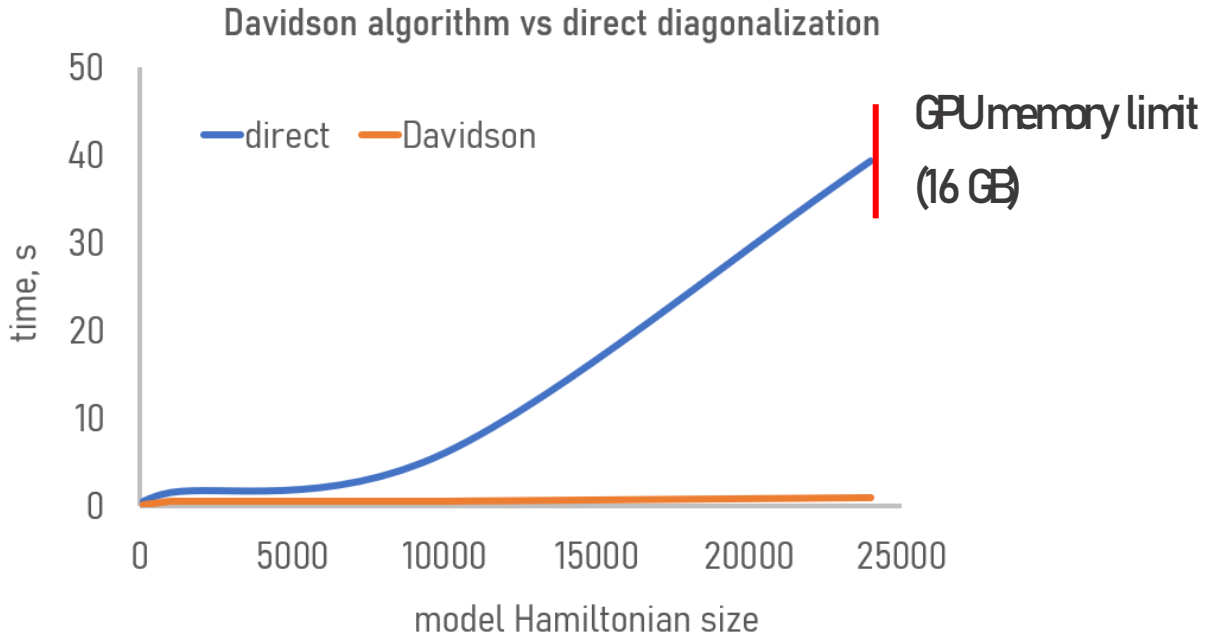
```
2.84655
3.05412
3.39660
3.53378
```

agrees with NEXMD and ORCA within 0.1%

# Davidson algorithm

- excited state Hamiltonian (CIS) scales as ~ (Nocc x Nvirt)$^2$
- trick is to never build CIS matrix in full – only projection in Krylov subspace using Davidson algorithm




GPU memory limit (16 GB)

DAVIDSON:

iter = 1

while iter < MAX iter:

$V = orthonormalize(V)$

$\sigma = AV$

$M = V^T\sigma$

$MX = \Lambda X \Rightarrow (\lambda, X)$

keep $(\lambda_i,\ldots \lambda_n)$, $(X_i,\ldots X_n)$

$r_i = \sigma Xi - \lambda_i V X_i$

if $\forall \|r_i\| <$ tol $\Rightarrow$ converged

return $(\lambda_i,\ldots \lambda_n)$, $(X_i,\ldots X_n)$

else:

for $\|r_i\| >$ tol:

$$s_i = \frac{r_i}{(D_i - \lambda_i)\|r_i\|}$$

V = (V, $s_i$)

if $m$ *in* $V_{n,m}$ > MAX size

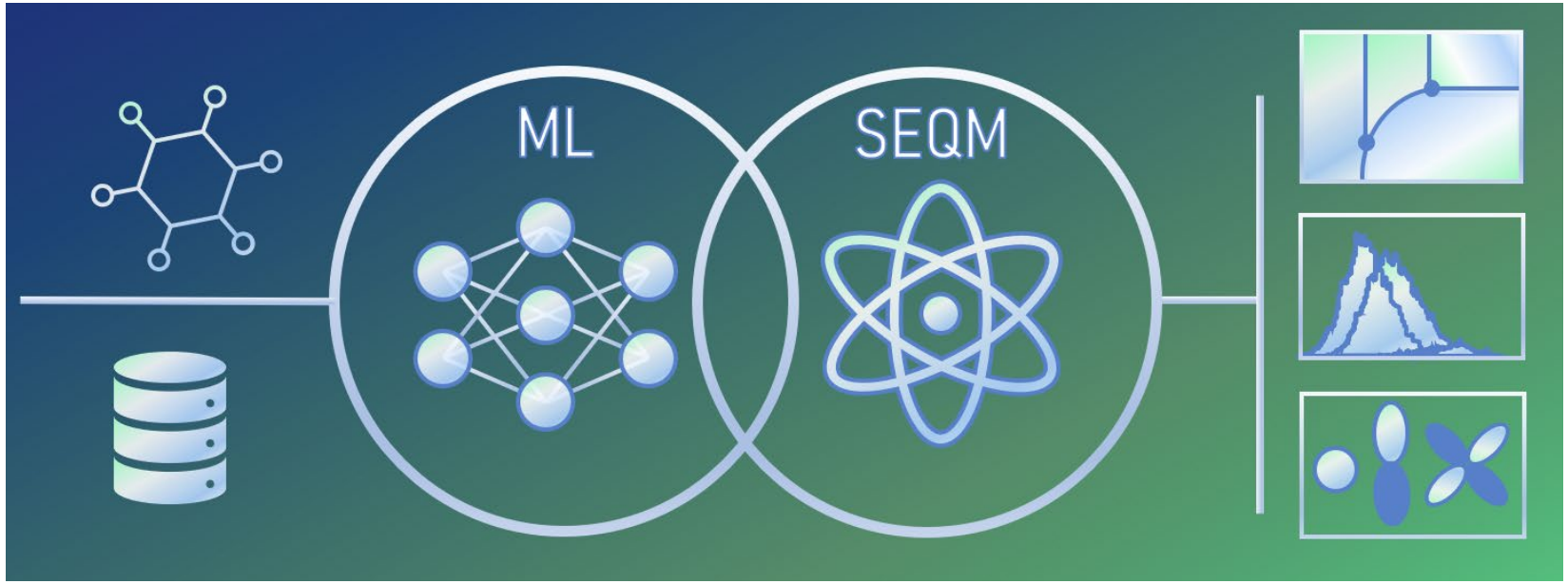
$V \longleftarrow VX$

continue

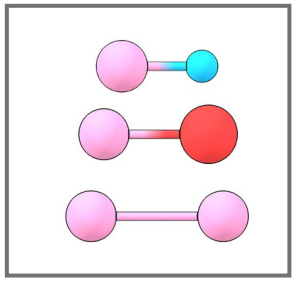
return $(\lambda_i,\ldots \lambda_n)$, $(X_i,\ldots X_n)$

END DAVIDSON

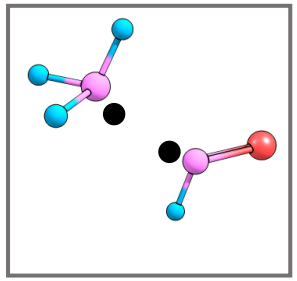
# Outlook



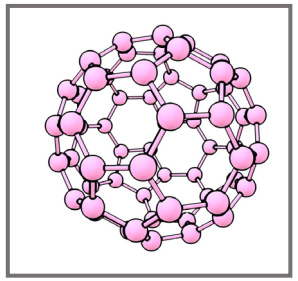

**Synergy of Semiempirical Models and Machine Learning in Computational Chemistry**
N. Fedik, B. Nebgen, N. Lubbers, K. Barros , M. Kulichenko, Y. W. Li, R. Zubatyuk, R. Messerly, O. Isayev, S. Tretiak. 2023, Journal of Chemical Physics (in press)



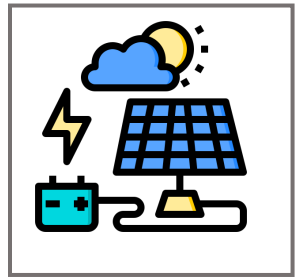
structure/bonding awareness



reactive and rare events



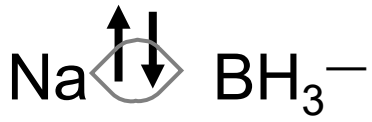
nanomaterials



photoreactions

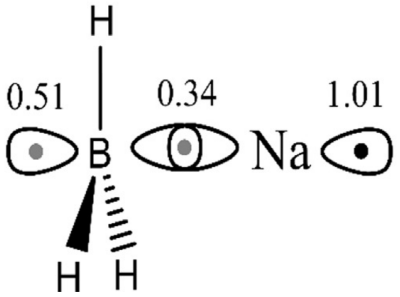
# $NaBH_3^-$ - Alternative Views

**covalent bond (electron-sharing)**




S. Pan, G. Frenking *Angew. Chem. Int. Ed.* **2020**, 59, 8756-8759

**2c-1e bond**

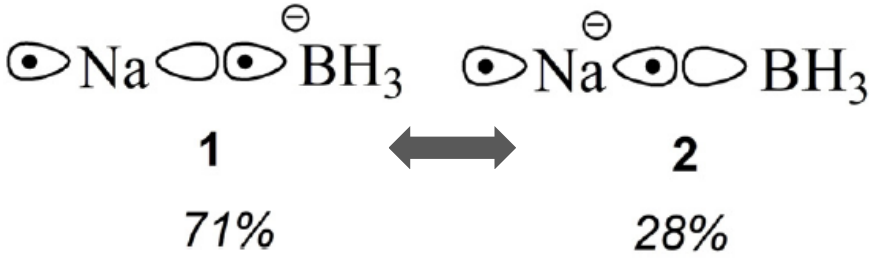



R. Pino-Rios, D. Inostroza, W. Tiznado *Angew. Chem. Int. Ed.* **2021**, 60, 12747–12753

**spin-polarized bond**


P. Salvador, D. E. Vos, I. Corral, D. M. Andrada *Angew. Chem. Int. Ed.* **2021**, 60, 1498–1502

**electrostatic + 2c-1e bond**

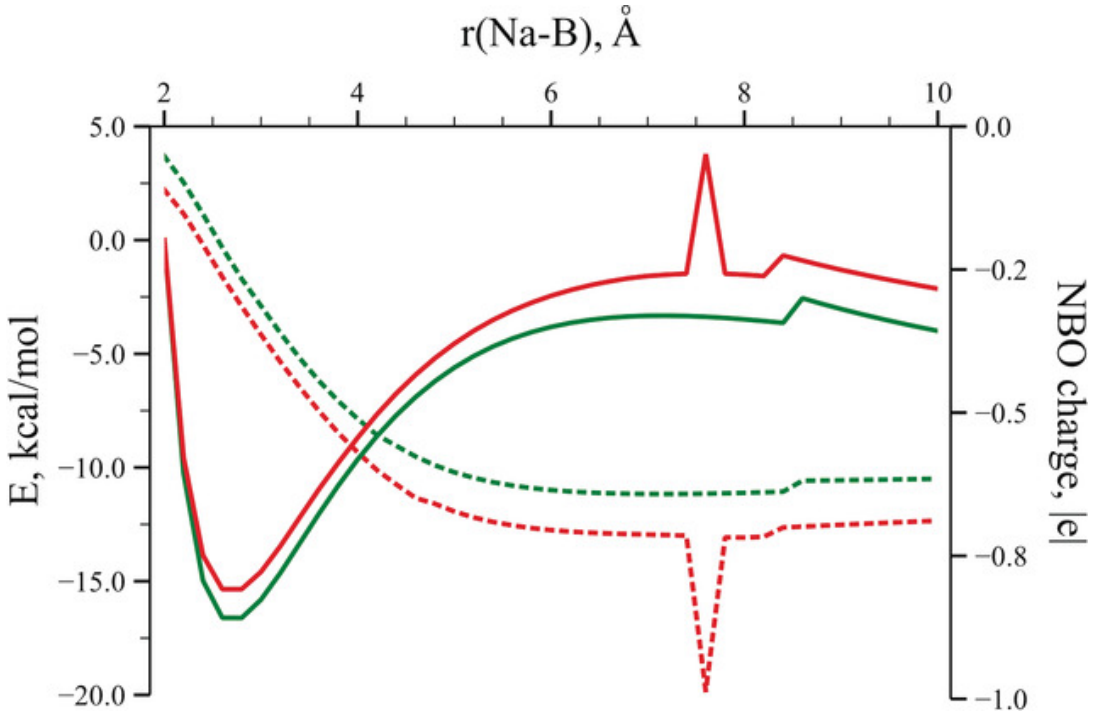


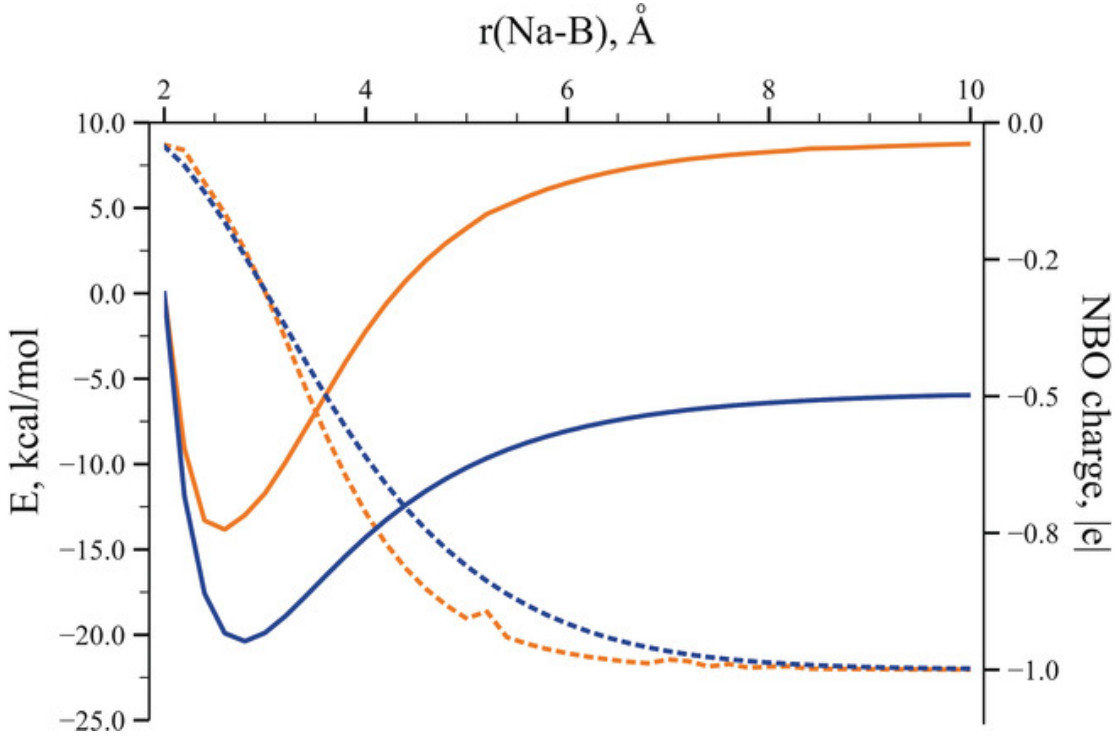

S. Radenkovic, S. S. Shaik, B. Braïda *Angew. Chem. Int. Ed.* **2021**, 60, 12723–12726

All interpretations agree that at large distances Na—B interaction is dative (dissociates into $Na^-$ and $BH_3$)

Discrepancies at the equilibrium are related to:

- Radical character of the wave function
- Pure semantics: all covalent bonds are electron-sharing at equilibrium. This does not exclude formation *via* dative mechanism.



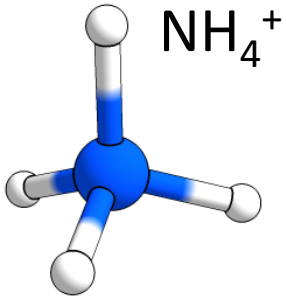

Pan and Frenking, DFT

upon separation, Na charge is partial

our description of wave function – CASSCF and UCCSD(T)

Na charge is -1

$NH_3 : \rightarrow \square H^+$




all bond are equal and electron-sharing